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Abstract

We have carried out a series of ab-initio calculations to investigate changes in the optical properties of Si quantum dots as a function of surface passivation. In particular, we have compared hydrogen passivated dots with those having alkyl groups at the surface. We find that, while on clusters with reconstructed surfaces a complete alkyl passivation is possible, steric repulsion prevents full passivation of Si dots with unreconstructed surfaces. In addition, our calculations show that steric repulsion may have a dominant effect in determining the surface structure, and eventually the stability of alkyl passivated clusters, with results dependent on the length of the carbon chain. Alkyl passivation weakly affects optical gaps of silicon quantum dots, while it substantially decreases ionization potentials and electron affinities and affect their excited state properties. On the basis of our results we propose that alkyl terminated quantum dots may be size selected taking advantage of the change in ionization potential as a function of the cluster size.

PACS numbers:

Functionalization of Si surfaces at the nanoscale might open the possibility of integrating solid state electronics with optical sensing techniques[1–5]. Although the structure of functionalized bulk surfaces is easier to determine experimentally[6, 7] than that of nanostructures, sensing applications may greatly benefit from the large surface to volume ratio of nanostructures and thus it is worth exploring their surface functionalization.

In spite of the significant success in using II-VI quantum dots as optical labels[8–10], research on Si quantum dots is pursued as an alternative to II-VI QDs, as Si does not require coating with layers of inert materials to avoid chemical toxicity; thus smaller chemical labels could be potentially obtained. However, Si QDs with homogeneous size distribution are much more difficult to synthesize than the ones of the II-VI family and their surface and optical properties are much more sensitive to oxidation [11–17] or reconstruction[18–20]. Nevertheless, Si, C, and SiC QDs are expected to be relatively bio-inert. Moreover, their surface may be stabilized and functionalized at the same time, without allowing an intermediate oxide layer to form[21–27].

Free standing Si QDs have been obtained with a variety of methods, for example: by etching of bulk Si [26, 28], by direct chemical synthesis[21, 22, 29], high pressure experiments[23, 24], laser driven pyrolysis[27] or aggregation of atoms in vacuum[30]. In all these cases, organic molecules are present at the surface either because directly incorporated in the synthesis reaction[21–24] or added after synthesis in other to stabilize and functionalize the surface[25–27].

The determination of structure and properties of surfaces of nanomaterials, represents a significant challenge to experiment and ab-initio simulations can provide help in complementing and interpreting experimental data. From a theoretical point of view, the influence of organic passivation on the electronic structure and optical properties of quantum dots has so far received limited attention. Early studies showed that the properties of quantum dots cannot be addressed with models based solely on the properties of the bulk[31]. The effect of replacing a single H atom by some organic groups at the surface of a Si dot was briefly addressed by Puzder et al. [20], and single chemical reactions involving unsaturated C chains and excited Si dots were recently investigated [32]. The full organic passivation of Si dots was explored by Z. Zhou et al with quantum chemistry methods. [15] However, the dependence of optical and electronic properties on the size of the dot and the length of the carbon chain were not addressed in Ref [15].

In this paper, we report a systematic study of the effects of an organic surface passivation on the optical and structural properties of Si quantum dots. In particular, we studied Si dots with reconstructed surfaces presenting only one dangling bond per surface atom. In this way, all facets could be terminated with the same type of chemical group. Our results show that alkyl passivation has a small effect (0.2 eV) on the optical gaps of Si dots as compared to H passivation, while significant changes occur in the position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), with respect to the vacuum level. At fixed core sizes, the magnitude of Alkyl-terminated-Si-dots gaps is similar to that of Si-rich SiC dots, suggesting that photo luminescence experiments are not sufficient to discriminate between alkyl terminated Si QDs and SiC QDs.

With respect to formation energies of alternative core structures, we find that passivation with methyl groups does not alter the relative stability of Si QS as compared with an H passivation. However, larger groups such as ethyl groups can contribute a steric repulsion energy as large as 0.08 eV per first neighbor pair. The effect of this steric energy can alter the energy balance in favor of different facets or different core structures depending on the length of the alkyl chain.

The rest of the paper is organized as follows: In Section I we describe the theoretical method employed in our calculations and the criteria used to select core and surface structures. In Section II we describe the results for the single particle properties and stability of alkyl passivated Si QDs. Finally we give our conclusions in Section III.

I. METHOD

Our *ab-initio* calculations were performed using Density Functional Theory within the Gradient Corrected Approximation of Perdew, Burke, and Ernzerholf [33] (PBE). We used a plane-wave pseudopotential method and the GP code[34]. The Si and C pseudopotentials were generated with the Troullier-Martins prescription[35], and we used a kinetic energy cutoff of 35 and 140 Ry to represent the single particle wave functions and charge density, respectively. The QDs were placed in a periodically repeated supercell, with the distance between replica larger than 12 Å. Geometry relaxations were performed until forces acting on all atoms were smaller than 10^{-4} a.u..

Previous work on Si and C has shown[20, 36, 37] that the HOMO-LUMO energy difference

underestimates the optical gap of QDs (e.g. by about 1.5 eV in Si), as compared with more accurate methods such as Quantum Monte Carlo (QMC). However, HOMO-LUMO and QMC gaps have been shown to provide the same qualitative trend as a function of the nanoparticle size and surface structure. Therefore here we refer to the "energy gap" or "gap" of the Si nanoparticle as the HOMO-LUMO energy difference and we expect the computed values to be shifted roughly by 1-2 eV in QMC calculations.

In principle, electron affinity A and ionization potential I should be evaluated as

$$\begin{aligned} A &= E(n) - E(n+1) \\ I &= E(n-1) - E(n) \end{aligned} \tag{1}$$

where $E(m)$ is the total energy of the system with m electrons and n is the number of electrons in a neutral system. Physically, A corresponds to the energy given by the system when an additional electron is added and I the energy provided to the system to remove an electron. Even though an electron is added to (taken from) the LUMO (HOMO) of the neutral system, neither A or I corresponds to the LUMO or HOMO energies because of polarization energies and self energy corrections[38]. However, it has been shown[38] that for Si QDs LUMO and HOMO energies behave qualitatively as -A and -I. As for large systems, like the ones reported in this study, it is cumbersome to calculate charged clusters with periodic boundary conditions, we will discuss HOMO and LUMO energies and relate them to the electron affinity or ionization potentials of Si dots.

A. Quantum dot core structure

The structure of the core of small Si nanocrystals is still a subject of debate. Even in cases where the core of the nanocrystal is assumed to be formed solely with Si atoms, it has been suggested that for 1 nm dots the lowest energy structure might not correspond to a diamond core [39]. In particular, small clusters with a core structure different from diamond (amorphous) were found to be more stable than crystalline ones because of a reduction of the surface energy[39]. As the energy difference between an amorphous structure and a crystalline one is proportional to the volume, it is expected that above a certain size the cost of the amorphous structure will overcome the surface energy gain and quantum dots become crystalline. However, because the number of amorphous configurations grows exponentially

with system size, it is probably impossible to determine precisely the size at which this transition occurs. Recently, Zhao et al. [40] have suggested that Si dots with icosahedral structure have lower energy than diamond dots for sizes smaller than 5 nm. Finally, in the cases where C containing compounds are used as reactants during the synthesis, one might consider the possibility that C is incorporated into the Si lattice, forming a cluster with the SiC structure. The presence of SiC QDs could offer an alternative explanation for light emission in the blue-ultraviolet observed experimentally. [12, 22, 41]

It is not the scope of this paper to find the lowest energy configuration of a Si cluster of a given size at $T = 0$ and we assumed here a core diamond structure for most of the Si nanoparticles studied. We will also discuss some results on icosahedral and amorphous quantum dots. In particular, we will compare core energy differences with steric surface energies. We will study Si_{20}, Si_{29}, Si_{66} and Si_{142} as a function of surface passivation, where Si_{20} is the smallest cluster with icosahedral symmetry.

B. Quantum dot surface structure

Under the assumption that the core of the dot is crystalline, the resulting surface structure will depend on the way one chooses to cut a three dimensional shape from the crystalline lattice. Historically, theoretical investigations have concentrated on nearly spherical shapes, which minimize the surface area and therefore are believed to minimize the surface energy. Some of the clusters obtained in this way have become prototypes for comparison of different theories and methods.[18–20, 32, 36, 39, 42–44] The resulting cluster structures have surface atoms with one or two dangling bonds. Specifically, in the case of a diamond core (111) and (110) facets will present one dangling bond per surface atom but (100) like facets will show two dangling bonds per surface atom. Therefore, it is in principle possible to put one or two hydrogen atoms on (100) facets depending on whether the surface is reconstructed or not [18–20]. In the case of hydrogenated unreconstructed (100) surfaces, the H atoms are close to each other and steric effects become more important as the size of the facet becomes larger[20, 45]. Unreconstructed (100) surfaces with passivants *larger* than H are very unlikely to form, as there is not enough room to place larger passivants (i.e. $-CH_3$ or $-C_2H_5$). Therefore, here we restrict ourselves to consider reconstructed clusters.

At variance with Zhou et al. [15] we choose to have the same type of chemistry everywhere

on the surface of the dot. That is, we considered clusters with reconstructed surfaces, one dangling bond per surface atom, and the same type of passivant on each facet. Methyl groups are easier to handle, because they can be added to the core structure without breaking the original symmetry of the cluster. Larger passivants break the original symmetry and are more difficult to place at the surface. For Si cores with Td symmetry, we chose configurations of surface passivants that retain all proper rotations (that is 12 of the 24 symmetry operations of the Td group). Even in this case, several different configurations are possible, and we chose that maximizing the distance between passivants at the surface, in order to minimize steric repulsions. Organic molecules can also be placed on clusters with icosahedral symmetry, where surface reconstructions are not expected. Steric repulsions can be estimated as the difference in energy between different configurations of the passivants on the surface.

II. RESULTS

We will present our results in two subsections. In the first one we will discuss the single particle properties that are affected by a passivation with alkyl groups, namely optical gaps, electron affinities, and ionization potentials. In the second subsection, we compare the core formation energy differences with energy differences due to steric effects of surface passivation.

A. Optical gaps and other spectral properties

In Figure 1 we show the evolution of the HOMO-LUMO gaps of Si quantum dots as a function of the surface passivation, for different core sizes. We observe small changes in the optical gaps as a function of surface passivation, in particular when the Si-H bond is replaced by a Si-C bond. Changes become negligible as the length of the C chain increases from 1 to 2 (calculations with the icosahedral Si_{20} core show very small changes when the third and fourth C atoms are added to the alkyl chain).

While the dependence of the gap on surface passivation is weak, in particular for the largest clusters, there are some effects to be noted. Surface passivation can have effects bigger than quantum confinement in some cases. If one compares, for example, the clusters derived from Si_{20} and Si_{29}, one finds that the the gap reduction due to a passivation change

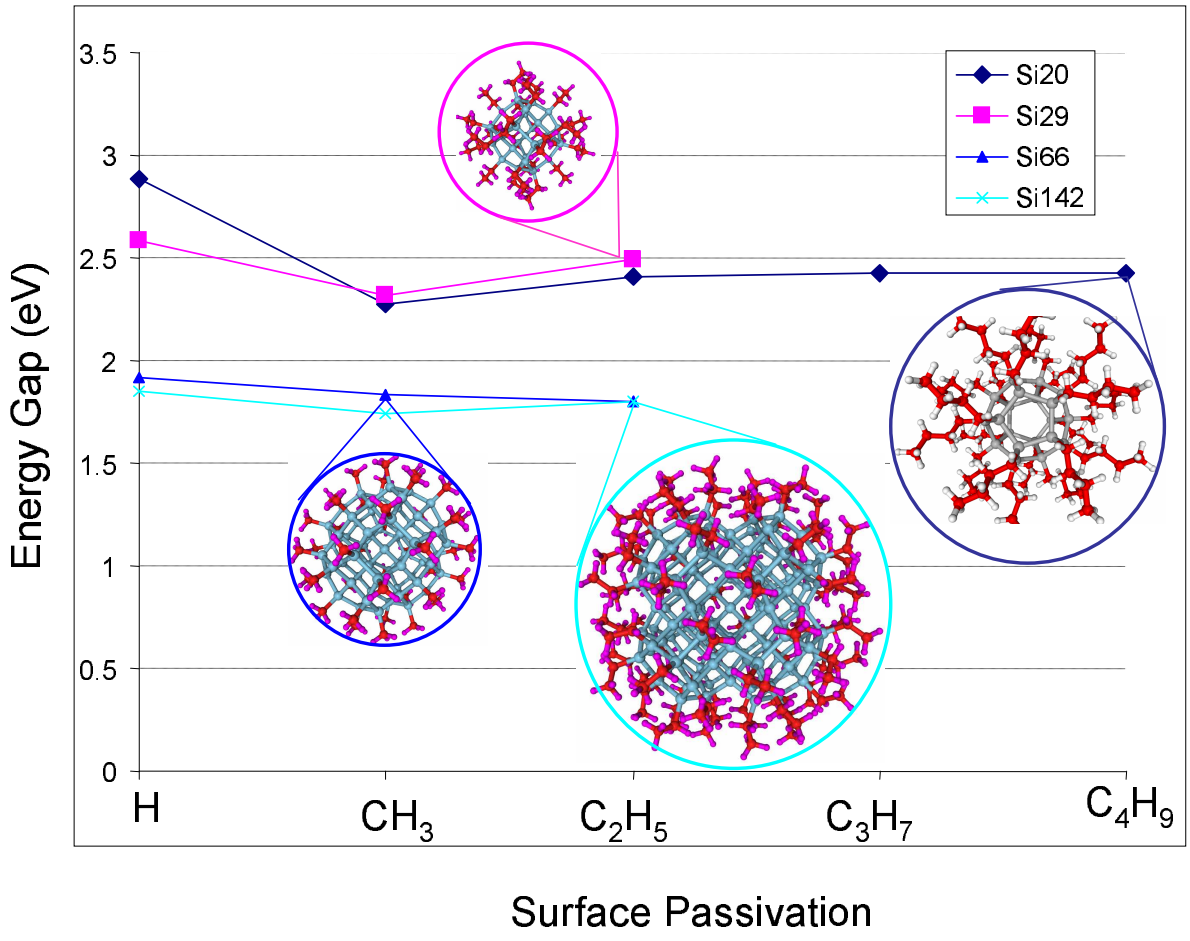

FIG. 1: (Color) HOMO-LUMO gaps (see text) of different Si clusters as a function of the passivation of the surface.

(from H to CH_3) has the same magnitude as the one due to size (see the hydrogenated case). Indeed the gap of Si_{20} is smaller than the one for Si_{29} for alkyl capped clusters. A similar effect is observed for Si_{66} and Si_{142}. We see in Figure 1 that in general the optical gaps are smaller for C passivated than for hydrogenated surfaces. This is similar to a reduction of quantum confinement (the HOMO and LUMO wave functions can "visit" more atoms in alkyl passivated clusters than in hydrogenated ones). The exception to the rule is Si_{29}, when CH_3 is replaced by C_2H_5. The reason for this might be related to other effects, such as surface strain.

While the changes in the gap value are not dramatic, much larger changes are found on the relative energy of the LUMO and the HOMO with respect to the vacuum. The HOMO can be related to the chemical potential of the system [50], and the LUMO provides an estimate

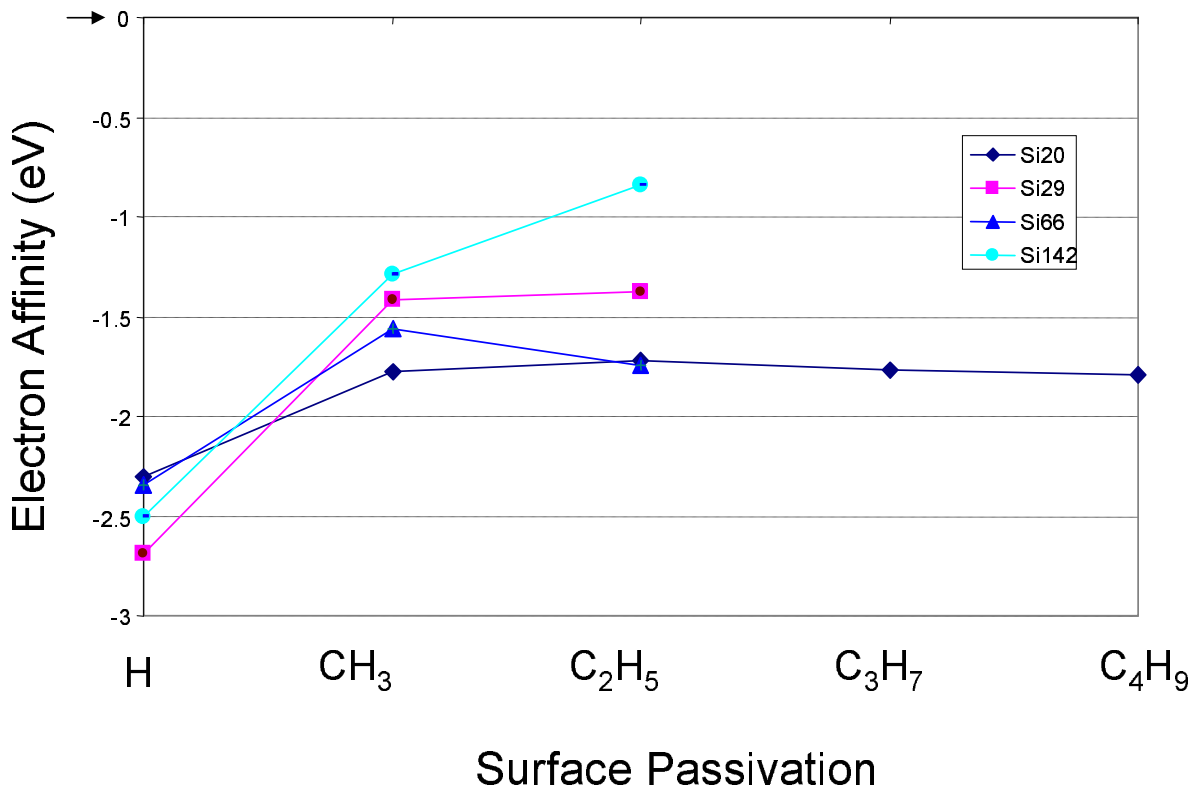

FIG. 2: (Color) LUMO energy (see text) of several Si clusters measured with respect to the vacuum potential as a function of surface passivation

of the electron affinity. In Figure 2 we show the evolution of the LUMO as a function of the length of the C chain (in our calculations we used the vacuum as a reference energy). We see that a change from H to CH_3 passivation has a drastic effect on the LUMO energy. Similar effects are observed in the HOMO energy (not shown). Several important points should be noted: i) There is a large shift in HOMO and LUMO energies when H is replaced by CH_3 and a smaller one when an additional C atom is added. ii) Changes in HOMO and LUMO positions are larger for larger dots than for smaller ones. iii) Calculations with Si_{20} show that the behavior of the LUMO is very flat when additional C atoms are added.

The dependence of the LUMO energy on the size of the dot and the size of the chain has an electrostatic origin. The results presented in Fig. 2 can be understood as follows. We argued in the discussion of Figure 1 that quantum confinement are weaker in alkyl terminated clusters than in hydrogenated ones at fixed core. Therefore, one could expect the energy of the LUMO to be decreased and that of the HOMO to be increased in alkylated clusters. However, there is an important additional effect: the formation of a dipole on the

surface of the cluster. In a simplified way, passivated clusters can be thought of as built from a series of concentric spheres, with H atoms belonging to the outermost sphere centered on the cluster. In the case of a hydrogenated clusters, H atoms are negatively charged, while in the case of an alkyl passivant, they are positively charged. As the total amount of charge of the system is zero, the potential should be constant outside the outermost "sphere" of charge. Thus an electron coming from the vacuum will see a constant potential until it encounters the H layer. Then it will see an attractive electrostatic potential if the neighbor is Si and a repulsive potential if the neighbor atom is a negatively charged C layer. Finally, it will see a potential drop due to the presence of Si atoms of the cluster core.

As a result of the shift of the LUMO energy with respect to the vacuum level, the number of bound states (with energy below zero) changes with alkylization. For example, in $Si_{29}H_{24}$ there are 15 bound states and for $Si_{29}(CH_3)_{24}$ this number is reduced to 8. The number of bound states increases as the length of the chain is further increased, but most of these "new" states have large overlap with the alkyl chains and little with the valence band wave functions localized on the silicon core. As a result of these changes in the electronic structure of Si QDs, although the optical gap does not change significantly for large dots, the absorption spectra 2 eV above the gap should be modified by a passivation with alkyl groups (which shift the relative position of the LUMO with respect to the scattering states).

Figures 1 and 2 suggest that it is easier to ionize a Si dot when it is passivated by alkyl molecules than when it is passivated with H atoms. Figure 2 shows that larger dots are more affected by alkyl passivation than smaller ones. In principle one could extract an electron from a quantum dot in a two step process: first, an electron hole pair is excited and, second, the electron is promoted to the vacuum either by another photon or by the decay of multiple excitons. For alkyl passivated quantum dots, both quantum confinement and the ionization energies are smaller for larger dots than small ones. Polarization energies are also expected to be smaller for large clusters[38]. This implies that large dots could be possibly charged under conditions which leave the small ones neutral. This property suggests a way of separating big charged dots from small neutral ones using eg. deflection in electric fields.

Zhou et al. [15] studied the influence of an organic passivation on Si_{29}. They passivate (111) facets with CH_3 radicals. However, instead of considering reconstruction of the (100)facets, they bridged with CH_2 groups the Si atoms that otherwise would form dimers.

In their case, they found a reduction of the gap of 0.6 eV as compared with the unreconstructed hydrogenated $Si_{29}H_{36}$. While the values of the gaps reported in Ref. [15] for the Si_{29} core are consistent with ours, we note that the type of passivation used in Ref. [15] might not be realistic for QDs larger than 1 nm because i) it involves a different chemical compound depending on the facet, and ii) there is not enough room to accommodate both CH_2 and CH_3 groups for a cluster with larger (100) facets (such as eg. Si_{142}).

B. Steric effects and core structures

We now consider what is the effect of an alkyl passivation on the formation energy of Si QDs.

1. Surface steric effects

Figure 3 shows two clusters with the same core structure and type of passivation. The difference between the two cases is the orientation of the ethyl groups on the (111) facets of the clusters. The configuration with lowest energy corresponds to the cluster denoted $Si29(C_2H_5)_{24}^{out}$ [see Fig. 3a)] where the ethyl groups are pointing outside the center of the (111) facet. The cluster $Si_{29}(C_2H_5)_{24}^{ins}$ is an alternative case where the ethyl groups are arranged cyclically closer to the center of the (111) facet. The difference in energy between these two structures is 0.96 eV. Since the cores of these two clusters and the position of the first carbon surface layer are identical, we attribute the difference in the formation energies of the clusters to steric repulsion of the ethyl groups. As there are 4 equivalent (111) facets in each cluster, we roughly estimate a 0.08 eV steric repulsion per ethyl pair.

We can then use this number to estimate steric effects for a much larger surface. Note that this is a lower bound to steric repulsion for clusters larger than 1 nm [51]. In a larger (111) facet, the number of first neighbors is 6 instead of 2. Most likely, in such a case, the C3 symmetry of the (111) surface is broken and the ground state configuration corresponds to all ethyl groups pointing in the same $(1\bar{1}0)$ direction. The intermolecular distances are similar to the ones shown in Fig. 3b, but without the possibility to relax to one side. Even though we have estimated a lower bound to the steric repulsion, this magnitude is already large enough to strongly influence and in principle determine the formation energy of each

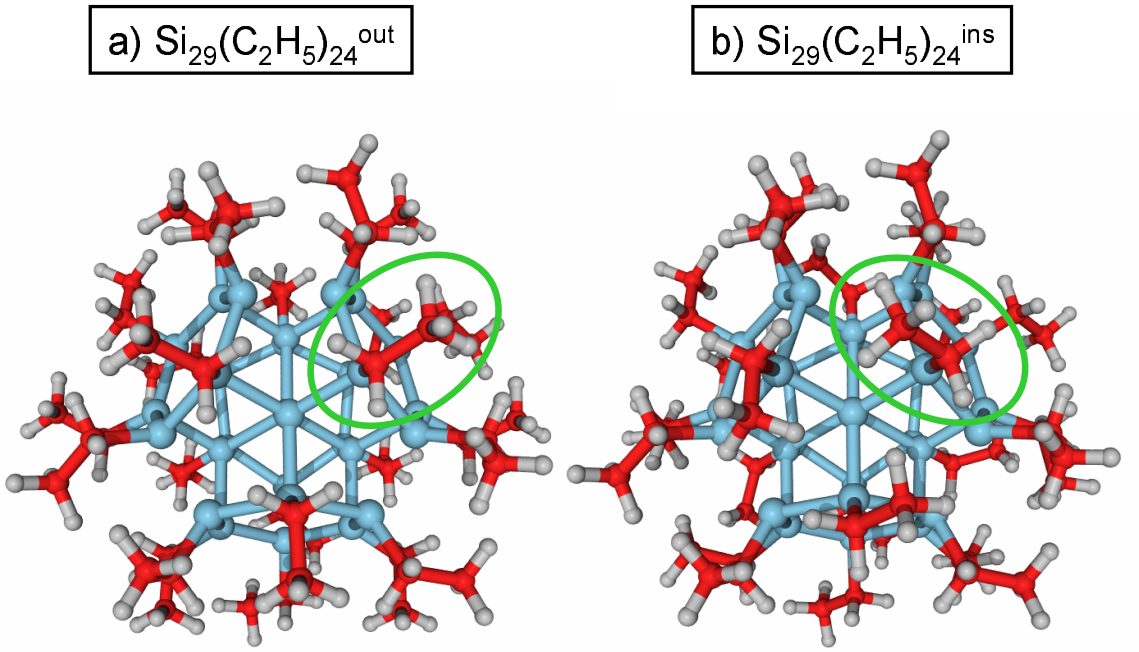

FIG. 3: (Color) $Si_{29}(C_2H_5)_{24}$ cluster with diamond core passivated with ethyl group for two configurations of the passivants: a) The ethyl groups are pointing outside the centers of (111) facets, b) the ethyl groups are oriented cyclically on the (111) facets.

type of facet, depending on the length of the C chain, and the flexibility of the bond between the passivant and the cluster.

We expect that surfaces with a large dangling bond density, eg. (111), might experience larger steric effects than (100) facets. The dangling bond densities on a reconstructed (100) surfaces is a factor $\sqrt{3}/2$ smaller than the one of (111) surfaces, allowing for more room to accommodate larger molecules. On the other hand, the dangling bond density of (110) surfaces is a factor $\sqrt{3/2}$ larger; but dangling bonds are accommodated in such a way that short passivants could avoid each other. Surfaces with rebonded steps[46] might offer lower dangling bond densities than the (100) at the expense of larger strain energies.

Steric effects will be dependent on the molecule attached to the surface. A compact surface passivation might also limit the chemical activity and the growth rate of the cluster along certain directions. These competing factors and energies could explain the variation

in shapes obtained experimentally depending on the synthesis method used[21–24].

2. Non crystalline cores

We will show in this section that the effects of an alkyl passivation on non-crystalline cores are similar to those on crystalline cores.

Quantum dots obtained from porous silicon[25, 26, 28] are likely to inherit the bulk crystalline structure. But for Si_{29} Draeger et al. [39] found two clusters with lower energy than the crystalline structure ($Si_{29}H_{24}$) we have considered so far. These two structures where denoted as $Si_{29}H_{24}^{nano1}$ and $Si_{29}H_{24}^{nano2}$. Here we investigate these structures with both hydrogenated and alkyl capped surfaces.

The changes in gaps and electron affinities of amorphous core clusters as a function of surface passivation are similar to the crystalline cluster cases. For $Si_{29}H_{24}^{nano1}$, $Si_{29}(CH_3)_{24}^{nano1}$ and $Si_{29}(C_2H_3)_{24}^{nano1}$ we obtained gaps of 3.01 eV, 2.33 eV and 2.25 respectively, while the LUMO energies are -1.91 eV, -1.45 eV and -1.50 eV.

With respect to formation energy differences we first considered methyl groups at the surface. For $Si_{29}(CH_3)_{24}^{nano1}$ we obtained a formation energy 1.08 eV lower than for the diamond core structure, while for $Si_{29}(CH_3)_{24}^{nano2}$ we obtained a formation energy 1.63 eV lower than the diamond reference. This result is very similar to the one found with H passivation[39] (1.13 eV and 1.58 eV respectively , at the LDA level of theory, with 35 Ry planewave cutoff)

While functionalization with methyl groups does not modify the conclusions reached in Ref.[39] for H passivated QDs, the effect of functionalization with longer chains is much more difficult to address. There is a unique way of adding methyl groups to the surface of silicon clusters. But studying the relative stability of clusters with longer alkyl chains is far more complex because there are three possibilities for the position of the next carbon atom in the alkyl chain. This implies that the number of configurations grows as $3^{(l-1)n}$ where l is the length of the carbon chain and n the number of dangling bonds on the surface of the cluster. For one of these configurations we find that $Si_{29}(C_2H_5)_{24}^{nano1}$ has a formation energy that is only 0.19 eV smaller than the crystalline reference $Si_{29}(C_2H_5)_{24}^{out}$. This smaller change is presumably a consequence of the fact that in the crystalline case [see Fig. 3a)] we were able to find a very good solution with many molecules avoiding each other. The fact that we did

not find a similar solution for the amorphous core does not mean it does not exist. Again, here we can estimate the total energy of the steric repulsions to be of the order of 1.4 eV.

3. Icosahedral quantum dots

Here we briefly discuss the case of a core with icosahedral shape. We have already studied in detail Si_{20} which is the smallest of the clusters of the icosahedral family[40]. Recently Zhao et al. [40] have suggested that icosahedral quantum dots have lower energy than the ones derived from the diamond lattice for diameters smaller than 5nm. Although interesting, we note here that such claims might be valid only for the specific magic numbers for which the perfect icosahedral shape can be formed.

A comparison between the stability of icosahedral and diamond dots is difficult because i) there is a large number of possibilities to consider for the surface of diamond cores [52] ii) the number of atoms (magic numbers) for which a perfect icosahedral cluster exist are different from the number of atoms for which nearly spherical diamond clusters can be constructed. A direct comparison of the ratio of surface energy to number of atoms might not be meaningful for clusters with different total number of atoms (i.e.: in Fig 2 of Ref. [40] the icosahedral quantum dot contains 18 % more atoms than the diamond dot). Finally, for alkyl passivated clusters, surface steric effects might be quantitatively more important than core formation energies.

While finding the absolute lowest energy configuration for a large number of Si atoms is probably impossible from a theoretical standpoint, we would like to compare some core-formation-energy differences with steric effects due to alkyl groups. According to Ref. [40] icosahedral clusters are energetically favored in the small size regime and in the absence of passivation. Here we consider the case of Si_{100}. In Figure 4 we compare two unpassivated Si clusters: one with icosahedral (4a) and the other with diamond structure (4b). Note that the diamond cluster is not spherical. As we could not find a 100 atom cluster with the diamond structure and a spherical shape, we just chopped atoms from a larger cluster trying to minimize the number of dangling bonds. Clearly, it is possible that another cluster with diamond core, the same number of atoms, and lower energy exists. As both clusters are unpassivated, the icosahedral symmetry is lost after relaxation, and the (100) facets of the diamond core reconstruct.

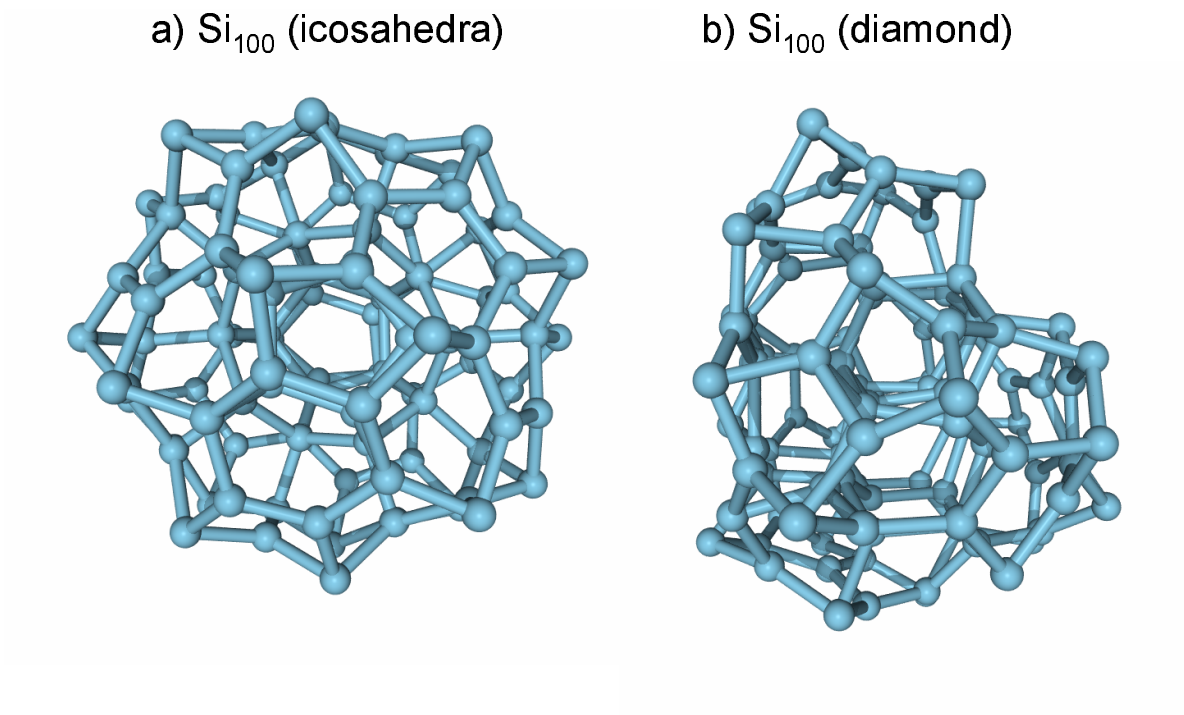

FIG. 4: (Color) Representation of two Si clusters with 100 atoms a) icosahedral structure b) diamond structure.

In spite of all these differences, the formation energies of these two clusters is very similar, the diamond cluster being 1.8 eV higher in energy than the icosahedral one. Although these results apparently confirm the claims made in Ref. [40], they should be interpreted with caution because of the following reasons: i) The energy difference per atom (18 meV $\simeq$ 200K) is smaller than room temperature, and smaller than the energy difference found between diamond and amorphous clusters for Si_{29} (see above). The calculated difference is much smaller than the one reported in Fig 3 of Ref. [40] for diamond Si_{558} and icosahedral Si_{600} (Note that the energy difference per atom were expected to decrease as the size of the cluster increases). ii) While there is a unique cluster related to the icosahedron shape, we have calculated only one of the several clusters that could be obtained from the diamond structure with 100 atoms. Therefore the difference we obtained in favor of the icosahedron structure is only an upper limit. iii) An alternative comparison can be done by removing 34 atoms from the icosahedral Si_{100} minimizing the number of dangling bonds left. The total energy of this truncated icosahedral cluster can be compared with diamond Si_{66} (which is a "magic number" with Td symmetry). Following this procedure one finds that the

energy difference is reversed in favor of the diamond structure and it is of the same order of magnitude. v) Finally, because the icosahedron surfaces are all (111) bulk-like facets and there are 60 surface dangling bonds on icosahedral Si_{100}, the energy difference between diamond and icosahedral shapes could be changed if passivants larger than H are at the surface.

Although the steric repulsions between ethyl or larger groups are small, we showed in the previous section that they can contribute as much as 0.08 eV per pair to formation energy differences. Thus, if all the interactions on the surface are considered, steric effects can eventually become more important than core formation energy differences for large clusters. As these interactions increase with the alkyl chain length, they eventually give a larger contribution than the the Si-C bond energy. It has been found that in a flat (111) surface a complete octadecyl passivation is not stable[47].

In conclusion, estimated steric repulsions due to alkyl groups are likely to be more important than core formation energy differences for sufficiently long passivants.

C. Comparison between SiC quantum dots and alkyl passivated Si dots

When C is added to synthesis reaction one might argue that SiC clusters could form instead of alkyl capped Si clusters[41]. Actually, some of the reactants that are claimed to produce Si quantum dots in high pressure experiments[23, 24] are similar to the ones used to grow SiC films in MOCVD[48] or SiC QDs in CVD [49]. In Figure 5 we compare the gaps of SiC QDs with different surface terminations, with those of silicon dots terminated with alkyl chains. The upper curve corresponds to C terminated unreconstructed SiC dots. The middle one corresponds to Si terminated reconstructed dots while the lower one corresponds to Si terminated SiC dots with and additional layer of Si atoms. The latter can be thought of as a SiC dots with defects (see Ref. [41] for details). Finally, the remaining points represent the clusters shown in Figure 1 (shown here as a function of the size of the core, using the same symbols as in Fig 1). We see that optical gaps of Si-rich SiC dots and alkyl capped Si dots are very similar suggesting that, unless radiative to non-radiative lifetimes are very different, photo-luminescence measurements can not be used to differentiate Si dots from Si-rich SiC dots below 2 nm. While Si and SiC have very different gaps in the bulk, our results show that they can be similar at the nanoscale depending on the surface termination.

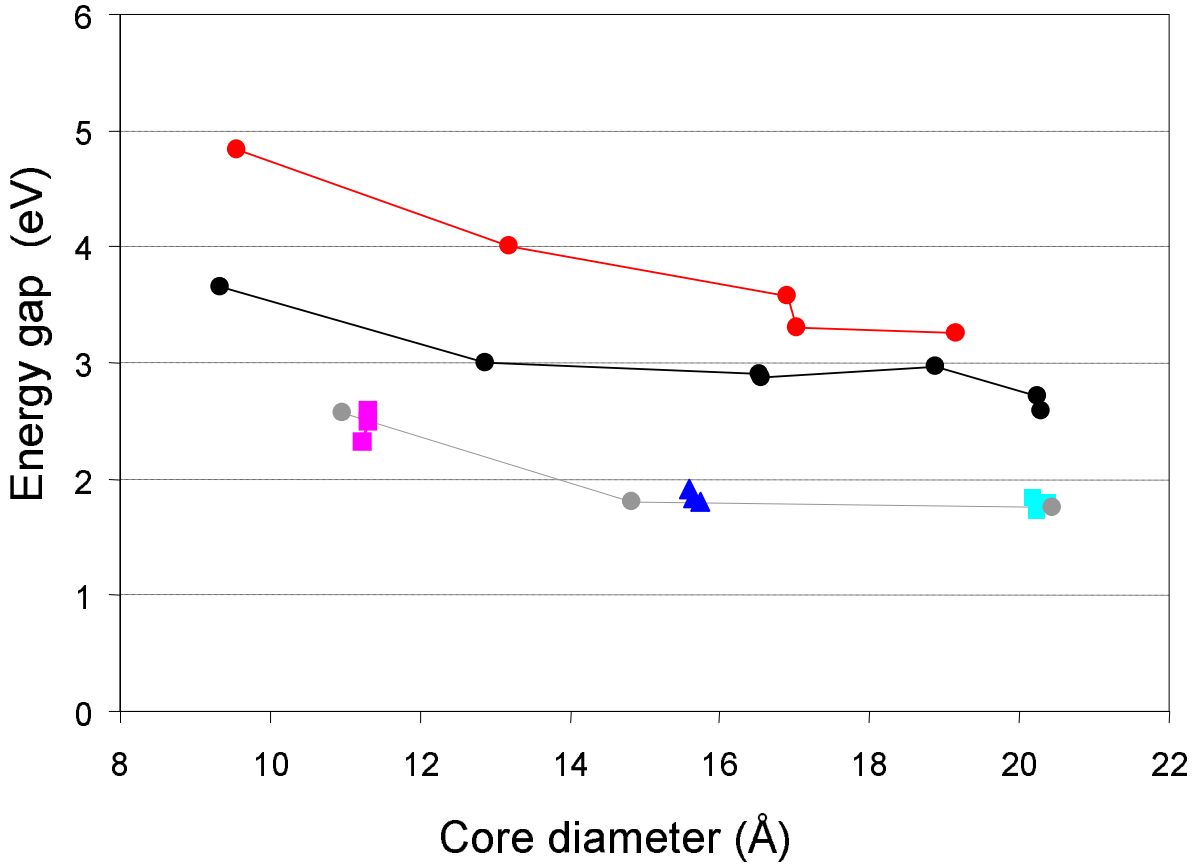

FIG. 5: Comparison of SiC QDs with alkyl capped Si dots. Red: carbon terminated unreconstructed SiC dots; black Si terminated reconstructed Si dots; gray Si-enriched SiC dots. Same symbols as in Fig. 1 for the Si dots.

Hydrogenated Si clusters, alkyl-capped Si dots, and Si-rich SiC dots have almost the same LUMO energies but the LUMO energies of alkyl terminated Si dots change as compared with Si-rich SiC dots. Thus, ionization energies or electron affinities may be used to physically distinguish SiC QDs from alkyl terminated Si QDs.

III. CONCLUSIONS

We have performed a systematic study of the electronic properties of alkyl terminated Si quantum dots. We find that the gap is weakly affected by organic passivation and that the electron affinity and ionization potential are properties more sensitive to surface structure. The magnitude of the change in energy of the HOMO and LUMO depends on the size of the dot, being more pronounced for 2nm dots than for smaller ones. Alkyl passivated Si dots

have different numbers of bound empty states, as compared to H passivated ones, suggesting different absorption spectra. Information on ionization energies and excitation spectra can be combined to differentiate alkyl terminated Si dots from Si-rich SiC dots. Moreover, we suggest that alkyl terminated Si clusters could be size selected taking advantage of the size dependence of the chemical potential (related to the HOMO energy). The changes in the gaps and band edge energies appear to be related to the polarity and chemistry of the surface and are similar irrespective of whether the core structure is diamond, amorphous or icosahedral.

Bare icosahedral quantum dots might not be the most stable form of Si clusters below 5 nm [40]. Instead we suggest that icosahedral quantum dots might be the most stable form of bare Si clusters for certain magic numbers, although the case of a lower energy amorphous cluster can not be ruled out. We have also estimated the magnitude of steric repulsions for ethyl groups on (111) facets. Our results show that steric repulsions might have a dominant effect in surface energies for Si clusters passivated with methyl or larger groups. Even for a passivation as small as the ethyl radical, the contribution of steric effects could be comparable to the difference in energy of alternative core structures.

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[50] As noted earlier, errors arise because of the approximation used here for the exchange correlation functional

[51] The lowest energy configuration in $Si29(C_2H_5)^{out}_{24}$ with all atoms facing the vacuum can not be repeated periodically in a larger facet without running into collisions with neighboring ethyl groups.

[52] For example, two atoms can be added at each one of the 6 (100) facets of Si_{323} (See Fig 2 Ref. [40]) eliminating of 12 dangling bonds while adding 12 rebonded steps to the cluster. As the cost of the rebonded step is much smaller than the cost of the dangling bond the *total* surface

energy should be reduced while the number of atoms increases.